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COMPOSITION FOR THE OXIDATION DYEING OF KERATIN FIBRES,  
CONTAINING A LACCASE, AND DYEING PROCESS USING THIS  
COMPOSITION

5           The invention relates to a composition for  
the oxidation dyeing of keratin fibres, and in  
particular of human keratin fibres such as the hair,  
comprising, in a medium which is suitable for dyeing,  
at least one heterocyclic oxidation dye and at least  
10 one laccase-type enzyme, as well as to the dyeing  
process using this composition.

It is known practice to dye keratin fibres,  
and in particular human hair, with dye compositions  
containing one or more oxidation dye precursors, in  
15 particular ortho- or para-phenylenediamines, ortho- or  
para-aminophenols, and heterocyclic bases, which are  
generally known as oxidation bases. These oxidation  
dyes (oxidation bases) are colourless or weakly  
coloured compounds which, when combined with oxidizing  
20 products, can give rise to coloured compounds and dyes  
by a process of oxidative condensation.

It is also known that the shades obtained  
with these oxidation bases can be varied by combining  
them with couplers or coloration modifiers, the latter  
25 being chosen in particular from aromatic meta-diamines,  
meta-aminophenols, meta-diphenols and certain  
heterocyclic compounds.

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The variety of molecules used as oxidation bases and couplers allows a wide range of colours to be obtained.

The so-called "permanent" coloration obtained  
5 by means of these oxidation dyes should moreover satisfy a certain number of requirements. Thus, it should have no toxicological drawbacks, it should allow shades to be obtained in the desired intensity and it should have good staying power with respect to external  
10 agents (light, bad weather, washing, permanent-waving, perspiration or rubbing).

The dyes should also allow grey hair to be covered and, finally, they should be as unselective as possible, i.e. they should allow only the smallest  
15 possible differences in coloration to be obtained along the same keratin fibre, which may indeed be differently sensitized (i.e. damaged) between its tip and its root.

The oxidation dyeing of keratin fibres is generally carried out in alkaline medium, in the  
20 presence of hydrogen peroxide. However, the use of alkaline media in the presence of hydrogen peroxide can have the drawback of resulting in substantial degradation of the fibres, as well as a decolorization of the keratin fibres, which is not always desirable.

25 The oxidation dyeing of keratin fibres can also be carried out using oxidizing systems other than hydrogen peroxide, such as enzymatic systems. Thus, it has already been proposed in US patent 3 251 742 and

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A first subject of the invention is thus a ready-to-use composition for the oxidation dyeing of

keratin fibres, and in particular of human keratin fibres such as the hair, characterized in that it comprises, in a medium which is suitable for dyeing,

- at least one oxidation dye chosen from heterocyclic oxidation bases and heterocyclic couplers, and
- at least one laccase-type enzyme,

the said composition being free of heterocyclic coupler chosen from indole, indoline, monocyclic pyridine and phenazine compounds and free of heterocyclic oxidation base chosen from 4,5-diamino-6-hydroxypyrimidine and 3,4-diaminohydroxypyrazole.

The ready-to-use dye composition in accordance with the invention leads to intense, chromatic colorations. The colorations obtained with the ready-to-use dye composition in accordance with the invention moreover show little selectivity and excellent properties of resistance both with respect to atmospheric agents such as light and bad weather and with respect to perspiration and the various treatments to which hair may be subjected (washing, permanent-waving).

A subject of the invention is also a process for the oxidation dyeing of keratin fibres using this ready-to-use dye composition.

The laccase(s) used in the ready-to-use dye composition in accordance with the invention can be chosen in particular from laccases of plant origin, of animal origin, of fungal origin (yeasts, moulds or

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fungi) or of bacterial origin, it being possible for the organisms of origin to be monocellular or multicellular. The laccase(s) used in the ready-to-use dye composition in accordance with the invention can  
 5 also be obtained by biotechnology.

Among the laccases of plant origin which can be used according to the invention, mention may be made of the laccases produced by plants which carry out chlorophyll synthesis, such as those mentioned in  
 10 patent application FR-A-2 694 018.

Mention may be made in particular of the laccases present in extracts of Anacardiaceae plants such as, for example, extracts of *Magnifera indica*, of *Schinus molle* or of *Pleiogynium timoriense*; in extracts  
 15 of Podocarpaceae plants, of *Rosmarinus off.*, of *Solanum tuberosum*, of *Iris sp.*, of *Coffea sp.*, of *Daucus carota*, of *Vinca minor*, of *Persea americana*, of *Catharanthus roseus*, of *Musa sp.*, of *Malus pumila*, of *Gingko biloba*, of *Monotropa hypopithys* (Indian pipe),  
 20 of *Aesculus sp.*, of *Acer pseudoplatanus*, of *Prunus persica* and of *Pistacia palaestina*.

Among the laccases of fungal origin, optionally obtained by biotechnology, which can be used according to the invention, mention may be made of the  
 25 laccase(s) obtained from *Polyporus versicolor*, from *Rhizoctonia praticola* and from *Rhus vernicifera* as described, for example, in patent applications FR-A-2 112 549 and EP-A-504 005; the laccases described in

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5 obtained from *Scytalidium*, from *Polyporus pinsitus*,  
from *Myceliophthora thermophila*, from *Rhizoctonia*  
*solani*, from *Pyricularia oryzae*, and variants thereof.  
Mention may also be made of the laccase(s) obtained  
from *Trametes versicolor*, from *Fomes fomentarius*, from  
10 *Chaetomium thermophile*, from *Neurospora crassa*, from  
*Colorius versicolor*, from *Botrytis cinerea*, from  
*Rigidoporus lignosus*, from *Phellinus noxius*, from  
*Pleurotus ostreatus*, from *Aspergillus nidulans*, from  
*Podospora anserina*, from *Agaricus bisporus*, from  
15 *Ganoderma lucidum*, from *Glomerella cingulata*, from  
*Lactarius piperatus*, from *Russula delica*, from  
*Heterobasidion annosum*, from *Thelephora terrestris*,  
from *Cladosporium cladosporioides*, from *Cerrena*  
*unicolor*, from *Coriolus hirsutus*, from *Ceriporiopsis*  
20 *subvermispora*, from *Coprinus cinereus*, from *Panaeolus*  
*papilionaceus*, from *Panaeolus sphinctrinus*, from  
*Schizophyllum commune*, from *Dichomitius squalens*, and  
from variants thereof.

The enzymatic activity of the laccases used in accordance with the invention and having

5 syringaldazine per minute at a pH of 5.5 and at a temperature of 30°C. One U unit corresponds to the amount of enzyme which produces an absorbance delta of 0.001 per minute at a wavelength of 530 nm, using syringaldazine as substrate, at 30°C and at a pH of 6.5.

According to the invention, the enzymatic activity is preferably determined in ulac units.

25            Among the pyrimidine derivatives which may be mentioned more particularly are the compounds described, for example, in German patent DE 2 359 399 or Japanese patents JP 88-169 571 and JP 91-333 495,

such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, and the addition salts thereof with an acid and pyrazolo-pyrimidine derivatives such as pyrazolo[1,5-a]pyrimidine-3,7-diamine,

- 5 2-methylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, pyrazolo[1,5-a]pyrimidine-3,5-diamine, 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine, 3-aminopyrazolo[1,5-a]pyrimidin-7-ol, 3-amino-5-
- 10 methylpyrazolo[1,5-a]pyrimidin-7-ol, 3-aminopyrazolo[1,5-a]pyrimidin-5-ol, 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol, 3-amino-7- $\beta$ -hydroxyethylamino-5-methylpyrazolo-
- 15 [1,5-a]pyrimidine, 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol, 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)-(2-hydroxyethyl)amino]ethanol, 2-[(7-amino-pyrazolo[1,5-a]pyrimidin-3-yl)-(2-hydroxyethyl)amino]-
- 20 ethanol, 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine and 2,5,N7,N7-tetramethylpyrazolo-
- [1,5-a]pyrimidine-3,7-diamine, and the addition salts thereof and the tautomeric forms thereof, when a tautomeric equilibrium exists.

Among the pyrazole derivatives which may be

25 mentioned more particularly are the compounds described in patents or patent applications DE 3 843 892, DE 4 133 957, DE 4 234 886, WO 94/08969, WO 94/08970, DE 4 234 887, FR 2 733 749, FR 2 735 685, such as



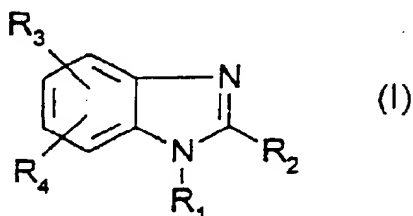
4,5-diaminopyrazole, 4,5-diamino-1-methylpyrazole,  
 1-benzyl-4,5-diaminopyrazole, 3,4-diaminopyrazole,  
 1-benzyl-4,5-diamino-3-methylpyrazole, 4-amino-1,3-  
 dimethyl-5-hydrazinopyrazole, 4,5-diamino-3-methyl-1-  
 5 phenylpyrazole, 4,5-diamino-1-tert-butyl-3-  
 methylpyrazole, 4,5-diamino-3-tert-butyl-1-methyl-  
 pyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole,  
 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole,  
 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole,  
 10 4,5-diamino-3-hydroxymethyl-1-methylpyrazole,  
 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole and  
 4,5-diamino-3-methyl-1-isopropylpyrazole, and the  
 addition salts thereof with an acid.

Among the heterocyclic couplers which can be  
 15 used in the ready-to-use dye composition in accordance  
 with the invention, mention may be made in particular  
 of benzimidazole derivatives, benzomorpholine  
 derivatives, sesamol derivatives, pyrazoloazole  
 derivatives, pyrroloazole derivatives, imidazoloazole  
 20 derivatives, pyrazolopyrimidine derivatives,  
 pyrazoline-3,5-dione derivatives, pyrrolo-  
 [3,2-d]oxazoline derivatives, pyrazolo[3,4-d]thiazole  
 derivatives, thiazoloazole S-oxide derivatives and  
 thiazoloazole S,S-dioxide derivatives, and the addition  
 25 salts thereof with an acid.

Among the benzimidazole derivatives which can  
 be used as heterocyclic couplers in the dye composition  
 in accordance with the invention, mention may be made

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more particularly of the compounds of formula (I) below, and the addition salts thereof with an acid:



in which:

- 5  $R_1$  represents a hydrogen atom or a  $C_1$ - $C_4$  alkyl radical,  
 $R_2$  represents a hydrogen atom or a  $C_1$ - $C_4$  alkyl or phenyl radical,  
 $R_3$  represents a hydroxyl, amino or methoxy radical,  
 $R_4$  represents a hydrogen atom or a hydroxyl, methoxy or  
 10  $C_1$ - $C_4$  alkyl radical;  
 with the proviso that:
- when  $R_3$  denotes an amino radical, then it occupies position 4,
  - when  $R_3$  occupies position 4, then  $R_4$  occupies position  
 15 7,
  - when  $R_3$  occupies position 5, then  $R_4$  occupies position  
 6.

Among the benzimidazole derivatives of formula (I) above which may be mentioned more  
 20 particularly are 4-hydroxybenzimidazole,  
 4-aminobenzimidazole, 4-hydroxy-7-methylbenzimidazole,  
 4-hydroxy-2-methylbenzimidazole, 1-butyl-4-hydroxy-  
 benzimidazole, 4-amino-2-methylbenzimidazole,  
 5,6-dihydroxybenzimidazole, 5-hydroxy-6-methoxy-

4,7-dihydroxy-1-methylbenzimidazole,

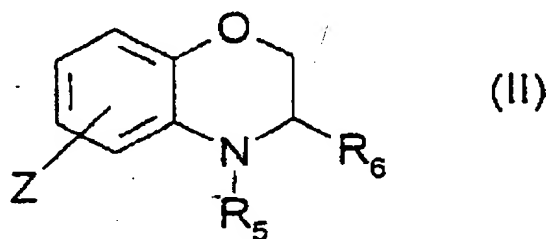
4,7-dimethoxybenzimidazole, 5,6-dihydroxy-1-methyl-

benzimidazole, 5,6-dihydroxy-2-methylbenzimidazole and

5 5,6-dimethoxybenzimidazole, and the addition salts thereof with an acid.

Among the benzomorpholine derivatives which can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention,

10 mention may be made more particularly of the compounds  
of formula (II) below, and the addition salts thereof  
with an acid:



in which:

15 R<sub>5</sub> and R<sub>6</sub>, which may be identical or different,  
represent a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl radical,  
Z represents a hydroxyl or amino radical.

Among the benzomorpholine derivatives of formula (II) above which may be mentioned more particularly are 6-hydroxy-1,4-benzomorpholine, N-methyl-6-hydroxy-1,4-benzomorpholine and 6-amino-1,4-benzomorpholine, and the addition salts thereof with an acid.

5 salts thereof with an acid:



- R<sub>7</sub> denotes a hydroxyl, amino, (C<sub>1</sub>-C<sub>4</sub>)alkylamino, monohydroxy(C<sub>1</sub>-C<sub>4</sub>)alkylamino or polyhydroxy(C<sub>2</sub>-C<sub>4</sub>)alkyl-

- R<sub>8</sub> denotes a hydrogen or halogen atom or a C<sub>1</sub>-C<sub>4</sub> alkoxy radical.

15 are 2-bromo-4,5-methylenedioxyphenol, 2-methoxy-  
4,5-methylenedioxyaniline and 2-( $\beta$ -hydroxyethyl)amino-  
4,5-methylenedioxybenzene, and the addition salts  
thereof with an acid.

20 be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in the following patents and patent applications: FR 2 075 583, EP-A-119 860, EP-A-285 274,

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EP-A-518 238, EP-A-456 226, EP-A-488 909, EP-A-488 248,  
and in the following publications:

- D.R. Liljegren Ber. 1964, 3436;
- E.J. Browne, J.C.S., 1962, 5149;
- 5 - P. Magnus, J.A.C.S., 1990, 112, 2465;
- P. Magnus, J.A.C.S., 1987, 109, 2711;
- Angew. Chem. 1960, 72, 956;
- and Rec. Trav. Chim. 1961, 80, 1075; the teachings of  
which form an integral part of the present patent  
10 application.

Pyrroloazole derivatives which may be  
mentioned most particularly are:

- 5-cyano-4-ethoxycarbonyl-8-méthylpyrrolo[1,2-b]-  
1,2,4-triazole,
- 15 - 5-cyano-8-methyl-4-phenylpyrrolo[1,2-b]-  
1,2,4-triazole,
- 7-amido-6-ethoxycarbonylpyrrolo[1,2-a]benzimidazole,  
and the addition salts thereof with an acid.

Among the imidazoloazole derivatives which  
20 can be used as heterocyclic couplers in the ready-to-  
use dye composition in accordance with the invention,  
mention may be made more particularly of the compounds  
described in the following patent applications and  
patents: US 5 441 863; JP 62-279 337; JP 06-236 011 and  
25 JP 07-092 632, the teachings of which form an integral  
part of the present patent application.

Imidazoloazole derivatives which may be  
mentioned most particularly are:

- 7,8-dicyanoimidazolo[3,2-a]imidazole,
  - 7,8-dicyano-4-methylimidazolo[3,2-a]imidazole,
- and the addition salts thereof with an acid.

Among the pyrazolopyrimidine derivatives which can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in the following patent application: EP-A-304 001, the teaching of which forms an integral part of the present patent application.

Pyrazolopyrimidine derivatives which may be mentioned most particularly are:

- pyrazolo[1,5-a]pyrimidin-7-one,  
- 2,5-dimethylpyrazolo[1,5-a]pyrimidin-7-one,  
15 - 2-methyl-6-ethoxycarbonylpyrazolo[1,5-a]pyrimidin-  
7-one,  
- 2-methyl-5-methoxymethylpyrazolo[1,5-a]pyrimidin-  
7-one,  
- 2-tert-butyl-5-trifluoromethylpyrazolo[1,5-  
20 a]pyrimidin-7-one,  
- 2,7-dimethylpyrazolo[1,5-a]pyrimidin-5-one, and the  
addition salts thereof with an acid.

Among the pyrazoline-3,5-dione derivatives which can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in the following patent

25 invention, mention may be made more particularly of  
compounds described in patent application JP 07 244 361  
and in J. Heterocycl. Chem. 16, 13, (1979).



5 may be made more particularly of the compounds described in the following documents:

- The heterocyclic oxidation dye(s), i.e. the  
15 heterocyclic oxidation base(s) and/or the heterocyclic  
coupler(s) preferably represent(s) from 0.0001% to 12%  
by weight approximately relative to the total weight of  
the ready-to-use dye composition, and even more  
preferably from 0.005% to 6% by weight approximately  
20 relative to this weight.

The ready-to-use dye composition in accordance with the invention can also contain, in addition to the heterocyclic oxidation dyes defined above, at least one benzenic oxidation base and/or at least one benzenic coupler and/or at least one direct dye, in particular to modify the shades or to enrich them with glints.

When they are used, these benzenic oxidation bases preferably represent from 0.0005% to 12% by weight approximately relative to the total weight of the dye composition, and even more preferably from 0.005% to 6% by weight approximately relative to this weight.

Among the benzenic couplers which may be additionally present in the ready-to-use dye composition in accordance with the invention, mention may be made in particular of meta-phenylenediamines, meta-aminophenols and meta-diphenols, and the addition salts thereof with an acid.

20                   When they are present, these benzenic  
couplers preferably represent from 0.0001% to 10% by  
weight approximately relative to the total weight of  
the ready-to-use dye composition, and even more  
preferably from 0.005% to 5% by weight approximately  
25 relative to this weight.

In general, the addition salts with an acid which can be used in the context of the dye compositions of the invention (oxidation bases and

couplers) are chosen in particular from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

The medium which is suitable for dyeing (or  
5 support) for the ready-to-use dye composition in accordance with the invention generally consists of water or of a mixture of water and at least one organic solvent to dissolve the compounds which would not be sufficiently water-soluble.

10 The pH of the ready-to-use composition in accordance with the invention is chosen such that the enzymatic activity of the laccase is sufficient. It is generally between 4 and 11 approximately, and preferably between 6 and 9 approximately. It can be  
15 adjusted to the desired value by means of acidifying or basifying agents usually used in the dyeing of keratin fibres.

The ready-to-use dye composition in accordance with the invention can also contain various  
20 adjuvants conventionally used in compositions for dyeing the hair, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures thereof, polymers, antioxidants, enzymes other than the laccases used in accordance with the invention, such  
25 as, for example, peroxidases or 2-electron-oxidoreductases, penetrating agents, sequestering agents, fragrances, buffers, dispersants, film-forming

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agents, preserving agents, opacifiers, thickeners and vitamins.

Needless to say, the person skilled in the art will take care to select this or these optionally  
5 additional compound(s) such that the advantageous properties intrinsically associated with the ready-to-use dye composition in accordance with the invention are not, or are not substantially, adversely affected by the addition(s) envisaged.

10           The ready-to-use dye composition in  
accordance with the invention can be in various forms,  
such as in the form of liquids, creams or gels, which  
may be pressurized, or in any other form which is  
suitable for dyeing keratin fibres, and in particular  
15 human hair. In this case, the heterocyclic oxidation  
dye(s) and optionally the additional oxidation dye(s)  
and the laccase-type enzyme(s) are present in the same  
ready-to-use composition, and consequently the said  
composition should be free of gaseous oxygen, so as to  
20 avoid any premature oxidation of the oxidation dye(s).

A subject of the invention is also a process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, using the ready-to-use dye composition as defined above.

25           According to this process, at least one ready-to-use dye composition as defined above is applied to the fibres for a period which is sufficient to develop the desired coloration, after which the

fibres are rinsed, optionally washed with shampoo, rinsed again and dried.

The time required to develop the coloration on the keratin fibres is generally between 3 minutes  
5 and 60 minutes and even more specifically between 5 minutes and 40 minutes.

According to one specific embodiment of the invention, the process includes a preliminary step consisting in separately storing, on the one hand, a  
10 composition (A) comprising, in a medium which is suitable for dyeing, at least one oxidation dye chosen from the heterocyclic oxidation bases and heterocyclic couplers as defined above, and, on the other hand, a composition (B) comprising, in a medium which is  
15 suitable for dyeing, at least one laccase-type enzyme, and then in mixing them together at the time of use, after which this mixture is applied to the keratin fibres.

Another subject of the invention is a multi-  
20 compartment dyeing device or "kit" or any other multi-compartment packaging system, a first compartment of which contains composition (A) as defined above and a second compartment of which contains composition (B) as defined above. These devices may be equipped with a  
25 means for applying the desired mixture to the hair, such as the devices described in patent FR-2 586 913 in the name of the Applicant.

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### DYEING EXAMPLE

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COMPOSITION	1	2
2,4,5,6-Tetraaminopyrimidine sulphate (heterocyclic oxidation base)	0.65	-
para-Phenylenediamine (benzenic oxidation base)	-	0.20
Resorcinol (benzenic coupler) /	0.30	-
2-Methoxy-4,5-methylenedioxyaniline monohydrochloride (heterocyclic coupler)	-	0.37
Laccase obtained from Rhus vernicifera at 180 units/mg, sold by the company Sigma	1.8	1.8
Common dye support (*)	(*)	(*)
Demineralized water qs	100 g	100 g

- Ethanol 20.0 g

- 10

4.8 g A.M.

pH = 6.5

Each of the ready-to-use dye compositions described above was applied to locks of natural grey hair containing 90% white hairs, for 40 minutes at a temperature of 30°C. The hair was then rinsed, washed  
5 with a standard shampoo and then dried.

The hair was dyed in the shades given in the Table below:

EXAMPLE	Shade obtained
1	Coppery mahogany light blond
2	light blond

In the dye compositions described above, the  
10 laccase from *Rhus vernicifera* at 180 units/mg, sold by the company Sigma, can be replaced with 1.0 g of laccase from *Pyricularia oryzae* at 100 units/mg, sold by the company ICN.

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